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Developments and interlaboratory study of the analysis of short-chain chlorinated paraffins

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ABSTRACT

To survey the conformity and quality of the results between laboratories for short-chain chlorinated paraffins (SCCPs) determination, we reviewed current and novel analytical methods and organized four worldwide laboratory exercises between 2011 and 2017.

Participants were requested to analyse test solutions and extracts of various matrices with their method of choice. Thirty-three laboratories participated (9–22 per round), of which 55–81% were able to submit data. Large differences in results between laboratories were found (CVs 23–137%) but results improved over time, while the levels in the test materials decreased. In the last round acceptable CV values (<25%) were obtained for the test solution. In the last round, results obtained by the GC–ECNI-LRMS technique varied most, which is disconcerting as this technique is most commonly applied. We strongly suggest to continue monitoring comparability of laboratories to assess consensus in SCCP analysis, with a focus on quantification procedures applied.

1. Introduction

Short-chain chlorinated paraffins (SCCPs) are polychlorinated *n*-alkanes with a carbon chain length of 10–13 carbon atoms and a chlorination degree by weight between 30 and 70%. The chlorination degree, chain length and chlorine atom distribution on the carbon chain can vary and thus also the physical properties, which make SCCPs suitable for a wide range of applications [1]. SCCPs are in general unreactive, flame retardive and lubricative compounds and, therefore in high demand. The cumulative chlorinated paraffin (CP) production volume is estimated to be 13 million tonnes (1935–2012) [2], which is ca. 10-fold higher than that of polychlorinated biphenyls (PCBs) [3], and production is ongoing. Because of their widespread presence in the environment as well as their persistent, bioaccumulative and toxic properties, SCCPs were in May 2017 classified as persistent organic pollutants (POPs) by the UN Environment Stockholm Convention with a few exemptions. They are also included in several regulatory lists such as the European Water Framework Directive, in order to monitor them regularly in the European aquatic environment. Therefore, an increasing number of laboratories will need to provide comparable and reliable results.

The determination of SCCPs is very challenging, mainly because of their response on current detection systems and their complexity (>7500 and 46 possible theoretical possible positional isomers and congener groups, respectively) [4]. SCCPs are normally analysed by gas chromatography (GC), but due to their aliphatic character, their response on current detection systems is relatively low compared to that of other persistent organic contaminants (for example 500 times lower than HCB with electron capture detector (ECD)) [5]. Separation of SCCP congeners (e.g. 2,3,4,5,6,7-heptachloroundedecane) remains unachieved by single-column GC or liquid chromatography (LC), resulting in a typical wide lump in the chromatogram and strong interference with other CPs such as medium-chain chlorinated paraffins (MCCPs) and compounds with similar retention times. Separation between congener groups, other fragmenting ions, and other compounds by mass spectrometry (MS) is difficult too, as at least a mass resolution of 20,000 (full width at half height) is needed [6]. For example,

Abbreviations: ∑SCCPs, Sum of SCCPs; ILS, Interlaboratory Study; AV, Assigned value; CV, Coefficient of variation.

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$C_{11}H_{17}^{37}Cl^{35}Cl_6$ and $C_{16}H_{29}^{35}Cl_5$ with electron-capture negative ionization MS (ECNI-MS) have a mass to charge ratio (m/z) of 395.9 and 396.1, respectively. Furthermore, quantification standards are badly needed [7] and certified reference materials (CRMs) for method validation and ensure accurate results are still unavailable.

Although SCCPs have been analysed since the early 1980s, concentrations remain reported as the sum of all SCCPs. Only a relatively small number of laboratories analyse these compounds. The acquisition and quantification procedures as well as results between laboratories vary greatly. To our knowledge, only two interlaboratory studies exist that assessed the variability associated between laboratories with different acquisition and quantification techniques; one comprising a test solution as well as a fish extract and conducted in 1999 [8], and one on a soil extract that was conducted in 2009 [9]. Those studies, in which six laboratories submitted results, reported between-laboratory coefficients (CV) between 47 and 209% for naturally contaminated environmental extracts.

Different instrumental and quantification techniques have been developed to attempt to cope with the challenges that arise with SCCP determination, with varying success. Here, we review the most currently applied as well as promising novel techniques. In addition, we evaluate the agreement in results between laboratories worldwide that apply these techniques.

2. Developments

An overview of the most commonly used approaches to analyse SCCPs is presented in Table 1. GC coupled to an ECNI-MS is the most commonly applied technique since the late 1990s [10]. With this technique the $[M-Cl]^-$ and $[M-HCl]^-$ ions are monitored for congener group specific analysis, enabling information on relative congener group patterns [11]. However, multiple injections are needed to monitor all ions and lower chlorinated CPs (CPs with less than 5 chlorine atoms) remain undetected [7]. Low-resolution (1000) single-quadrupole MS (LRMS) is most commonly used [12], for which extensive clean-up and fractionation procedures are essential to minimize interferences with other halogenated compounds [13]. Interferences with longer chained CPs and simultaneously formed fragments and adduct ions [10,13] remain problematic with the LRMS. Identification procedures have been developed to distinguish between MCCPs and SCCPs [11,14] but are time-consuming and require multiple injections. With the developments in MS such as the time of flight (ToF) and Orbitrap, the required resolution (>20,000) can be achieved, and all ions are monitored in one injection [15].

The response on ECNI is dependent on the chlorine content of SCCPs [13]. Therefore, the SCCPs pattern of quantification standards and sample should match as closely as possible [10]. To achieve this, multiple SCCP mixtures with different chlorination degrees are injected as quantification standards. Reth et al. [11] applied a linear relationship between the total response factors and the chlorine contents for SCCPs, improving precision of the results, which is the most commonly applied quantification procedure, covering quantification for SCCPs with a chlorine content of 51–70%. Another, less frequently used method is the monitoring of four ions fragment ions and the use of multiple linear regression for SCCPs (Cl content 49–67%) in sediment or water [16,17]. However, this method requires specialised personnel.

Two other ion monitoring techniques simpler and faster compared to the congener group specific analysis are monitoring only the $[Cl_2]^-$ and $[HCl_2]$ ions by GC–ECNI-LRMS [18], and monitoring the precursor and production common to most CPs by GC electron ionization tandem MS (GC–EI-MS/MS) [19]. The GC–EI-MS/MS technique achieves response with 0.25–0.5 ng injected and is less dependent on chlorination degree compared to ECNI. Disadvantages of these two techniques are that congener group pattern information is lost, ions monitored are not specific for CPs and differentiation between SCCPs and MCCPs and LCCPs fails [19]. Therefore, they are only suitable for SCCP analysis in samples in which longer chained CPs are absent.

A technique faster than ECNI that does provide information on the carbon chain length is the carbon skeleton method based on dechlorination (Csk-GC–EI-MS/MS and LRMS) [20]. Only a few ions need to be monitored, simplifying calibration and quantification although information on chlorination content is lost. With this method sensitivity is increased by decreasing chromatographic separation and lower chlorinated CPs are also detected. Response is less chlorine dependent and, therefore, the choice of standard is less crucial. However, some Pd catalysts might degrade longer

Table 1
Overview of most commonly applied instrumental and quantification techniques for short-chain chlorinated paraffins.

Instrument	Monitored ions by MS	Advantages	Disadvantages
GC–ECNI-MS (LRMS and HRMS) [10,11]	$[M-Cl]^-$ and $[M-HCl]^-$	- Congener group specific analysis	- Analysis limited to SCCPs with Cl_{5-10} atoms - Response chlorine dependent - LRMS: Risk of interferences - HRMS: Difficult to operate
GC–ECNI-LRMS [18]	$[Cl_2]^-$ and $[HCl_2]$	- Response less chlorine dependent than ECNI - Few ions monitored	- Risk of interferences - Congener group specific analysis impossible - Failure of differentiation with MCCPs and LCCPs
GC–EI-MS/MS [19]	The two most abundant ions for fragmentation of SCCPs	- Response less chlorine dependent than ECNI - Few ions monitored	- Congener group specific analysis impossible - Failure of differentiation with MCCPs and LCCPs
Csk-GC–EI-MS (MS/MS and LRMS) [20]	Two most abundant ions for fragmentation of *n*-alkanes (C_{10-13})	- Response independent of chlorine content - Few ions monitored	- Failure of differentiation with MCCPs and LCCPs - Risk of overestimation
Chlorine enhanced APCI-QToF-MS [25]	$[M+Cl]^-$	- Fast acquisition time - Response less chlorine dependent than ECNI - Analysis of SCCPs with Cl_{3-12} atoms - Congener group specific analysis	- Difficult to setup
GC × GC–ECNI-TOF-MS [24]	$[M-Cl]^-$ and $[M-HCl]^-$	- Separation congener specific - Congener group specific analysis	- Difficult to setup and operate - Analysis limited to SCCPs with Cl_{5-10} atoms

APCI Atmospheric Pressure Chemical Ionization; Csk Carbon Skeleton; ECNI Electron Capture Negative Ionization; HRMS High resolution MS; LCCPs Long-Chain Chlorinated Paraffins; LRMS Low Resolution MS; MCCPs Medium-Chain Chlorinated Paraffins; NA Not Applicable; SCCPs Short-Chain Chlorinated Paraffins; μECD Micro Electron Capture Detector.

chained alkanes present in the sample, resulting in an overestimation of SCCPs [21].

Comprehensive two dimensional gas chromatography (GC × GC) enables improved separation in chromatography. In 2005, Korytár et al. developed a GC × GC method for SCCPs [22], achieving at least some separation of congener groups. However, at that time even GC × GC was unable to offer sufficient resolution to separate all individual SCCP congeners. In addition, suitable congener standards needed to identify the congeners were not available. Many individual SCCP congeners commercially available have a different chlorination pattern than congeners present in technical SCCP mixtures [22]. When technical mixtures are produced, the chlorination starts from the centre of the alkane chain, proceeds on alternating C-atoms and chlorination of the end-C atoms does not occur [7]. The commercially available congener standards all have chlorinated end-C atoms [7]. Ten years later, Muscalu et al. developed a method with GC × GC coupled to a micro-ECD (GC × GC–μECD) [23], while Xia et al. developed a GC × GC–ECNI-TOF-MS method [24], in which separation between the congeners improved. The GC × GC–ECNI-TOF-MS combines improved separation with the required high resolution. GC × GC is, however, still difficult to operate routinely and requires some time to get all parameter settings right.

The method of Bogdal et al. [25] focussed only on high resolution MS and totally omitted the use of chromatographic separation. This resulted in very fast acquisition time (2 min). They used direct introduction by an LC sampler to introduce SCCPs to a high resolution TOF-MS mass spectrometer (APCI-QToF-MS). By using dichloromethane as a dopant, nearly exclusive $[M+Cl]^-$ ions are formed, which enhances selectivity and detectability. They also developed a new quantification procedure, using a mathematical algorithm to deconvolute CP congener group patterns in the samples into a combination of patterns in the standard mixtures injected. Just like ECNI, the set of standards needs to be large to mimic the SCCP pattern in the analysed samples as closely as possible.

In 2016 Gao et al. [26] developed a method for which the calculated concentration depends less on the distribution profile of SCCP congeners in the standards. This method also enabled the detection of SCCPs with Cl_{1-4} and acquires information on both carbon chain length and chlorine distribution. SCCPs are transformed to deuterated *n*-alkanes by deuterodechlorination. These deuterated n-alkanes are then completely separated by GC and molecular ions $[M]^+$ of the deuterated n-alkanes reflecting the chlorine distribution of SCCPs, are monitored.

New developments include the increasing interest of commercial companies to manufacture suitable individual congeners as analytical standards and the possible production of suitable CRMs. Just recently new SCCP congeners have been offered commercially (Chiron, Norway). While CRMs are unavailable yet, SCCPs recently have been identified in CRMs certified for other compounds, elsewhere [9,27]. Recently, the European Commission Joint Research Centre (EC-JRC) Directorate F: Health, Consumers and Reference Materials (Geel, Belgium) has investigated the suitability of various candidate certified reference materials. CRMs are essential to validate instrumental techniques to ensure accurate levels and consensus between laboratories. Ideally, a new CRM could include data on individual SCCP congeners. A series of new interlaboratory studies in food items has been initiated in 2017 by the European Reference Laboratory for POPs, Freiburg, Germany.

3. Interlaboratory exercises

3.1. Experimental design

Following a QUASIMEME workshop on the analysis of CPs in Ostend, Belgium, 2010, four interlaboratory exercises were organized for the determination of SCCPs in test solutions and environmental extracts, designed in a step-wise way (Table 2). The test materials provided were test solutions of SCCP mixtures in undisclosed concentrations and extracts of naturally contaminated environmental samples. Round 1 offered a test solution to the participants, consisting of a SCCP mixture with 55.5% Cl content by weight (Dr. Ehrenstorfer, Germany). Round 2 comprised a pike-perch extract from The Netherlands. In round 3 two samples were prepared based on the extraction of a sediment: one sample was the raw extract, the other sample consisted of the extract after clean-up. Round 4 consisted of four different test materials. The test solution was a SCCP mixture with 58.7% Cl, obtained by mixing SCCP 63% Cl and 55.5% Cl. The house dust extract was prepared from a reference material from National Institute for Standards and Technology (NIST), coded SRM 2585, still uncertified for SCCPs. The soil extract prepared from BCR-481, a reference material from the EC-JRC Directorate F: Health, Consumers and Reference Materials, coded, also uncertified for SCCPs. The fish extract was pooled yellow eel (fillets) from various locations in The Netherlands.

As the focus was on results obtained by the instrumental techniques and quantification procedures applied, uncertainties related to extraction and clean-up procedures were eliminated in rounds 1, 2 and 4 by providing cleaned and fractionated extracts. In round 3 the effect of different clean-up procedures was investigated by dividing the sediment extract into two parts (ca. 40:60) of which one (Sediment B, Table 2) still needed to be cleaned-up and fractionated. Details of the samples and their preparation per round are provided in the supporting information (Appendix A) and summarized in Table 2. After preparation the extracts were screened for the presence of SCCPs and in rounds 3–4 also screened for the presence MCCPs and toxaphenes by using GC × GC-μECD and APCI-

Table 2
Interlaboratory exercises overview.

#	Provided extract	Sample preparation[a]	Type exercise	Provided standard[a]
1	Test solution	SCCP mix 55.5% Cl[b]	Quantify	SCCP mix 51.5% Cl
2	Fish	PLE + Al_2O_3 + 1.6% H_2O Silica	Quantify	SCCP mix 51.5% Cl
3	Sediment A	A: PLE + 40% H_2SO_4 Silica (w/w) + 1.6% H_2O Silica	A: Quantify	SCCP mix 63% Cl
	Sediment B	B: PLE only	B: Cleanup & quantify	
4	2× Test solution	SCCP mix 58.7% Cl[b]	Quantify, provide relative abundance of congener group patterns	SCCP mix 63% Cl
	2× House dust	PLE + 40% H_2SO_4 Silica (w/w) + 2× 1.6% H_2O Silica		
	2× Soil	PLE + 40% H_2SO_4 Silica (w/w) + 2× 1.6% H_2O Silica		
	2× Fish	PLE + 40% H_2SO_4 Silica (w/w) + 2× 1.6% H_2O Silica		

PLE: Pressurized liquid extraction.
More information is provided in Supplementary data Appendix D.
[a] All standards, test solutions and extracts were provided in iso-octane.
[b] Chlorination degree unknown to participants.

QToF-MS. All standards, solutions and extracts were prepared in iso-octane and ampouled in 1–3 mL glass vials.

Participants received the ampoules with test materials and quantification standards, guidelines and report forms. They were asked to provide three independent analytical results of the total concentration of SCCPs (∑SCCPs) in μg/g iso-octane, using the provided quantification standard and an analytical method of their choice (e.g. acquisition, calibration and quantification). In round 3 they were requested to clean up sediment extract B with their method of choice. In round 4 they were asked to provide triplicate results of duplicate ampoules. Participants were encouraged to use their own quantification standards and, in round 4, provide additional information such as chlorination degrees and relative abundance of congener groups. Furthermore, they were requested to provide a short description of the analytical method used (rounds 1–4) and quantification procedures (round 4).

3.2. Data assessment

The data assessment was carried out according to the principles of the QUASIMEME proficiency testing organisation [28]. As determining SCCPs in the environment is challenging, more 'relaxed' settings for the interlaboratory study could be considered (e.g. 40–50% CV as acceptable instead of 25%). However, SCCPs are now classified as POPs and will be included in the Global Monitoring Program of the Stockholm Convention that has certain requirements. As also stated by van Leeuwen et al. [29], the minimum requirement for international monitoring programs (e.g. the Joint Monitoring Programme of the Oslo and Paris Commissions) is that participating laboratories can jointly observe changes in trends of 50% in a ten-year period, which can be achieved by a maximum CV of 25%. Hence, we believe using the standard QUASIMEME settings (25% CV as acceptable) are also the best choice for the SCCPs. A higher CV would include a risk for laboratories to be satisfied with their performance at a too early stage.

The reported concentrations were analysed using the “Normal Distribution Approximation” of the Cofino model, for which the details are provided elsewhere [30]. This model provides a consensus value based on all submitted data, a between-laboratory coefficient of variation (CV) and an inclusion rate. The latter gives the percentage of the data that contributes to the consensus value. The model has been shown to be very robust and therefore unsensitive to extreme values [31]. The consensus value of the datasets was used as the assigned value. The standard deviation for proficiency assessment was calculated using the QUASIMEME methodology [32], using a proportional error of 12.5% and a constant error (CE) of 0.025 μg/g for all determinands, except for the biota extract in round 4, for which a CE of 0.005 μg/g was used. In addition to the results quantified with the provided standard, in rounds 3–4 enough participants ($n > 7$) submitted results quantified with their own standards. Therefore, that data was assessed as a separate dataset.

3.3. Results

In total 33 different laboratories from 14 different countries participated (Appendix B). Per round the number of participants and submitted results varied, as described in a flow diagram in Appendix C. Briefly, 13–20 laboratories participated per round of which 9–13 were able to submit data (completion rates 55–81%). Some laboratories reported two datasets, obtained with different instrumental techniques. Although the number of participating laboratories is relatively small compared to interlaboratory studies on other POPs such as UNEP ($n > 100$) [29], it is higher than the previous SCCPs interlaboratory studies that comprised different acquisition and quantification methods ($n = 6–7$) [8,9].

An overview of methods applied is given in Appendix D. In brief, participants applied various analytical techniques to determine SCCPs ($n = 4–6$ per round, Fig. 1), and within the same analytical technique different monitoring ion techniques as well as quantification methods (Fig. 3, Graph E–H). GC–ECNI-LRMS was the most commonly applied technique (43–58%). In round 4, the use of the GC–EI-MS(/MS) was unreported while the recently developed APCI-QToF-MS technique became popular. The decreasing use of GC–EI-MS(/MS) might be due to the outliers obtained by this technique in round 3 (Fig. 2). All columns used for single column GC and as first column for GC × GC were non-polar, with dimethyl- or phenylmethylpolysiloxane stationary phases. As second column for GC × GC polar to semi-polar columns were used.

3.3.1. Laboratory performances

The results of the laboratory performances are shown in Table 3 and Figs. 2 and 3. Within- and between-laboratory variations, and where possible, accuracy and precision were evaluated, for which the results all indicated an improvement in agreement in results

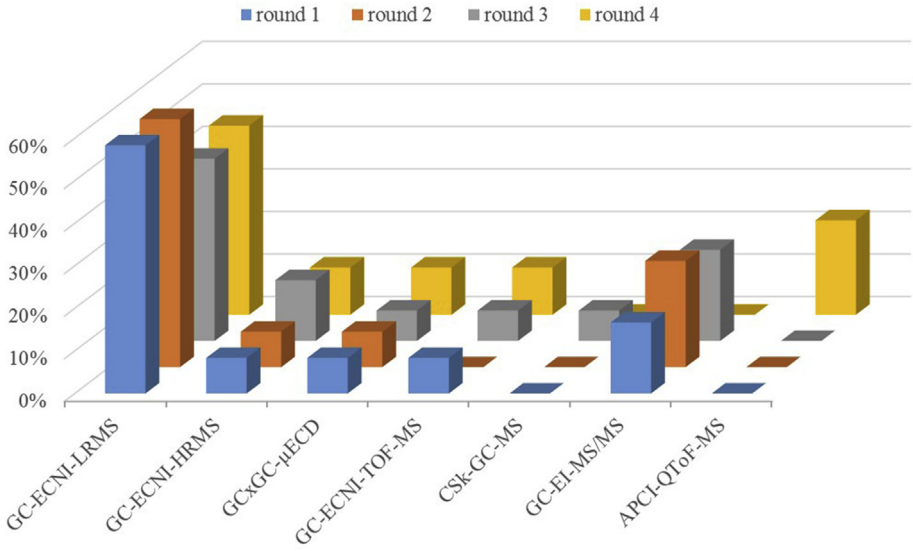

Fig. 1. Reported instrumental techniques, normalized per round.

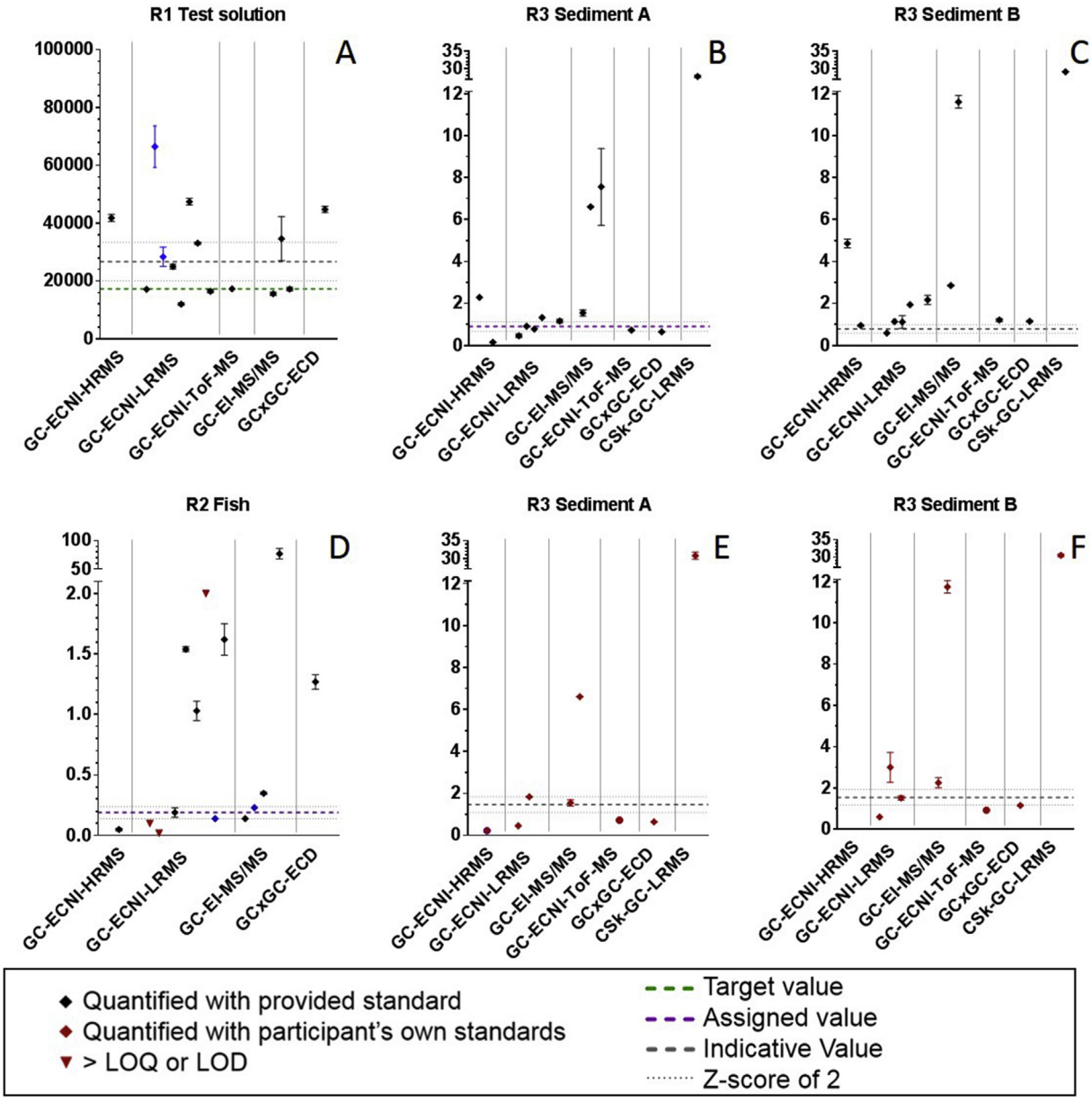

Fig. 2. Applied instrumental techniques, target and assigned values, z-scores and reported ΣSCCPs concentrations in interlaboratory study rounds 1–3, determined either with provided quantification standard (indicated in black) or with participant's own quantification standards and own quantification methods (indicated in different colours).

between the rounds over time. Almost every laboratory submitted results in triplicate which gave information on the internal laboratory variation. In general, >83% of the laboratories had a within-laboratory variation of 1–15%. The reported within-laboratory variations above 15% were obtained by either GC–EI-MS/MS or GC–ECNI-LRMS. Apart from the fish extract in round 4, within-laboratory variations decreased over time, even though the levels of SCCPs in the test materials simultaneously decreased. This result clearly indicates improved analytical performance. The relatively high within-laboratory variation for the fish extract was probably due to the low SCCPs levels (AV 0.02 μg/g) in this sample. Dust and the other fish extract (round 2) also contained low levels of SCCP, which were for some laboratories below the limit of quantification (LOQ).

Accuracy of the assigned value could be evaluated to some degree for the test solutions, as the concentrations were known. The difference between the assigned values and the true concentration (1.92 μg/g; 'target value' in Graph A Fig. 3) for the test solution in round 4 (30–48%) was smaller than the difference found in round 1 (54%), and compared to the previous interlaboratory study (−30 + 310%) [8], suggesting improvement.

Apart from the fish extract in round 2, the inclusion rate of the data (the percentage reflecting how many data points are included in the inter-laboratory CV, Table 3) of all rounds appears to be acceptable (>62%), showing that the between-laboratory CV is representative for the entire group of participants. Although large between-laboratory CVs were found (23–137%, Table 3), the CVs decreased over time, while the levels (reported consensus concentrations) were lower too, suggesting improvement in performance. The relatively high CVs observed for both biota extracts in rounds 2 (137%) and 4 (50–86%) are probably due to the very low concentrations (AV 0.19 and 0.019 μg/g respectively) in these samples. Comparing results of interlaboratory studies of which the data are assessed by different methods should be done with

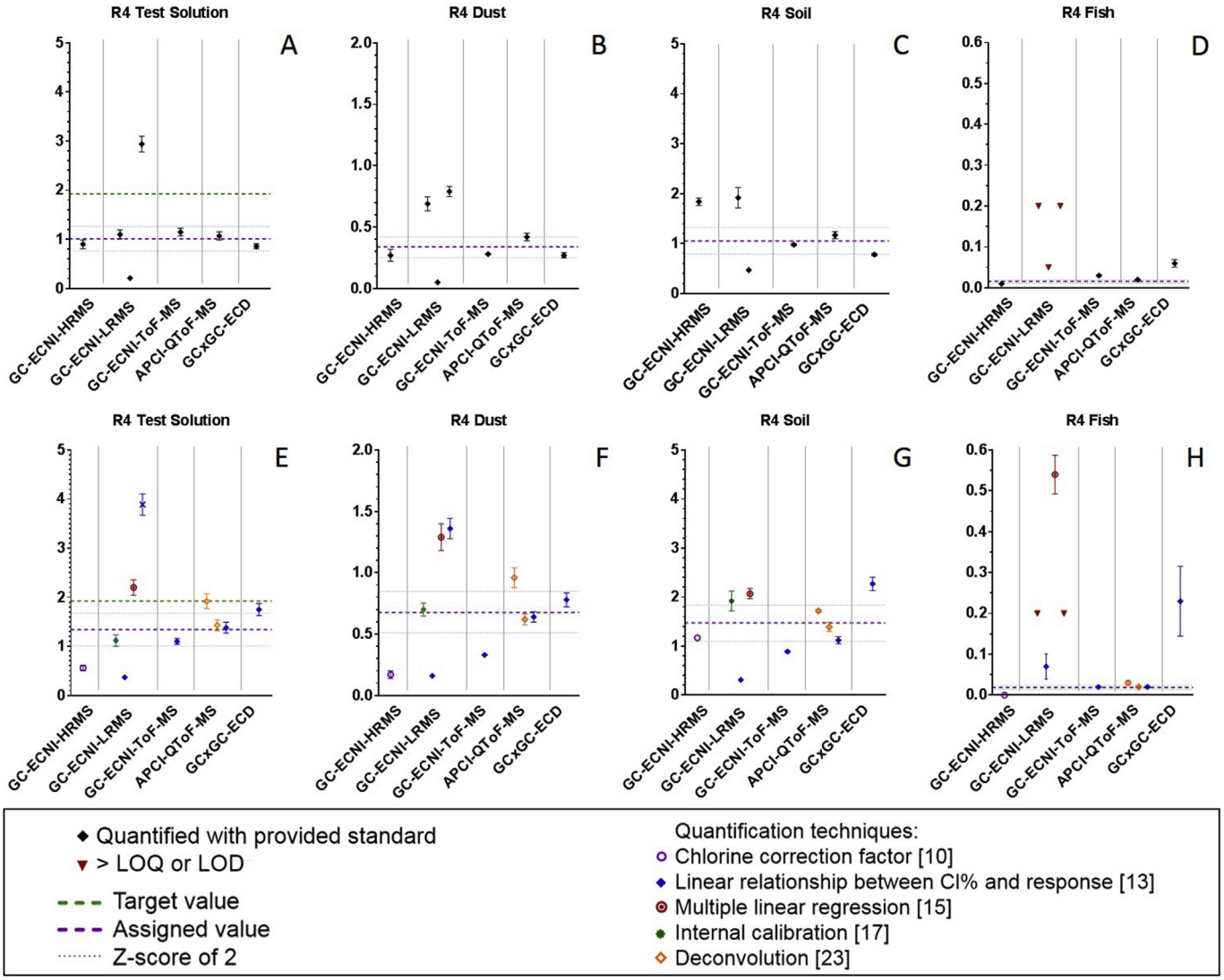

Fig. 3. Applied instrumental techniques, target and assigned values, z-scores and reported ΣSCCPs concentrations in interlaboratory study round 4, determined either with provided quantification standard (indicated in black) or with participant's own quantification standards and own quantification methods (indicated in different colours).

Table 3
Assigned values, between-lab coefficients (Between-lab CVs) and submitted results (*n*) per test material.

Round		Assigned value (μg/g)	Indicative value (μg/g)	Between-lab CV (%)	Inclusion rate (%)	Calculated Cl % and CV	Within lab CV (%)	n/n[a]
Quantified with provided standard								
#1	Test solution 55.5% Cl	NA	26,700	56	76	NA	3–22	14/0
#2	Fish	0.19	NA	137	50	NA	2–23	10/3
#3	Sediment A	0.91	NA	80	63	NA	0.32–24	36/0
	Sediment B	NA	1.93	86	62	NA	0.19–27	36/0
#4	Test solution 58.7% Cl	1.01	NA	23	65	58.6–64.7 (4%)	5–10[b]	42/0
	House dust	0.34	NA	68	72	55.7–63.7 (5%)	1–18[b]	42/0
	Soil	1.05	NA	47	69	54.9–65 (7%)	1–11[b]	35/0
	Fish	0.02	NA	86	71	56.2–67.5 (7%)	3–24[b]	25/9
Quantified with participant's own standard								
#3	Sediment A	NA	1.11	117	67	NA	0.42–21	23/0
	Sediment B	NA	2.00	86	67	NA	1–24	23/0
#4	Test solution 58.7% Cl	1.34	NA	50	72	58.6–64.7 (4%)	5–10[b]	60/0
	House dust	0.68	NA	72	82	55.7–63.7 (5%)	1–19[b]	60/0
	Soil	1.47	NA	47	80	54.9–65 (7%)	1–11[b]	53/0
	Fish	0.02	NA	50	53	56.2–67.5 (7%)	6–46[b]	43/9

CV coefficient of variation.
[a] Number of submitted results above limit of detection (LOD) or limit of quantification (LOQ) (first number), and number of submitted results below LOD and LOQ (second number), see text.
[b] Based on three measurements of duplicate ampoules.

caution. Taking that into account, compared to the CV of the only other interlaboratory study comprising a test solution (44%) [8], the CVs for the test solution of this study were about equal or lower (23–56%), while the number of participants were twice as high. All CVs for the results for the environmental extracts of this study were much lower than the CV for the soil extract (209%) of the other interlaboratory study [9]. The soil extract used in round 4 was the same soil extract as in the other study, while the final concentration was twice as low and the, the CV was a 4-fold lower.

3.3.2. Potential factors affecting between-laboratory CV

While the between-laboratory CV was unaffected by using own clean-up methods of choice (round 3 in Table 3), different instrumental techniques and quantification procedures probably did (Fig. 2). For example in round 3, results obtained by CSk-GC–EI-LRMS technique were a factor of approximately 30 higher than the AV. The reason for the large difference is unclear to us, CSk-GC–EI-LRMS is known to provide accurate quantification of *n*-alkanes [33] and scored well in the previous interlaboratory study [9]. Maybe the chlorine content was unknown to the participants, adding uncertainty to the SCCP calculation [34].

Another example is the GC–EI-MS(/MS) technique. While results obtained by this technique for the test solution (round 1) agreed well with the assigned value (z-score <2), some results obtained by GC–EI-MS(/MS) in the environmental extracts were identified as extreme outliers (rounds 2 and 3). For example in round 3, three out of the four participants applying GC–EI-MS(/MS), reported concentrations 10–30 fold higher than those of participants using other ionization modes and instruments. In round 4 concentrations obtained by GC–MS(/MS) were lacking and the highest values, obtained by GC–ECNI-LRMS, were now a 4-fold higher (Fig. 3). In the past, LRMS measurements could exceed those of HRMS by more than 300% [8]. In the present study, results obtained by ECNI-MS were in closer agreement, suggesting an increasing consensus in concentrations between LRMS and HRMS measurements when operated in the ECNI mode. However, in round 4 the highest variety between results was found when GC–ECNI-LRMS was used. This is disconcerting as this technique is the most commonly applied one. Further research in investigating the differences in SCCP concentrations measured by GC/MS operated in EI mode and ECNI mode is recommended.

As SCCPs remain unseparated by single column GC, we anticipated that between-laboratory CVs would remain unaffected by the choice of column and GC parameters. Increasing ion source temperatures in ECNI-MS is believed to decrease the relative abundances of the monitored ions [35] and could lead to different results than when compared to lower ion source temperatures (150°C). In this study either an ion source of 150°C or 200°C was applied. However, no relationship between ion source temperatures and difference in reported concentrations was identified.

In general between-laboratory CVs for results obtained with the quantifications standards of the participants themselves were similar to those obtained with the provided standard (Table 2). Exceptions were the provided cleaned sediment extract A in round 3 and test solution in round 4, for which the CV increased 1.5- and 2-fold when participants used their own standard for quantification, respectively.

In terms of accuracy, the % error of the assigned value of the true value for results quantified with participant's own standards was smaller compared to that when quantified with the provided interlaboratory study standard. This is possibly due to the difference in chlorine content in the test solution (58.7%) and provided standard (63%), suggesting how essential it is to have a similar chlorination degree between the standards and the sample and/or using a chlorine response correction factor [11]. Likewise, low variation was found in the results obtained by ECNI-MS techniques for the provided cleaned sediment extract quantified with the provided standard (sediment A Fig. 2), in which the chlorinated degree and pattern in sediment extract was very similar (both 63%).

Interfering compounds such as longer chain CPs, toxaphenes and PCBs were absent in most extracts in rounds 3 and 4, except for the dust extract and biota extract in round 4. In these extracts MCCP levels were approximately a 5-fold higher than SCCP levels (results obtained by APCI-QToF-MS). When MCCPs are present in higher levels than SCCPs, they might interfere with the analysis when using LRMS. However, the presence of MCCPs in the dust and biota extracts did not lead to substantially higher reported concentrations by LRMS compared to HRMS.

Reported relative abundancies of the congener groups were dependent on the technique used, as different abundancies were reported per technique (Appendix F). Relative abundancies reported in published studies should therefore be compared with caution.

4. Conclusions and recommendations

SCCP analysis is still challenging. A relatively small number of laboratories participated in the interlaboratory studies, many different techniques were applied and differences between laboratories were substantial. Nonetheless, these differences are decreasing over time, indicating an improved analytical performance, with in the last round an acceptable CV (<25%) obtained for the test solution.

Fish was found to be the most difficult environmental extract to analyse, probably because of the very low SCCPs levels. The results obtained by the novel APCI-QToF-MS technique agreed well with both the consensus value and the true value in the last round, while the results of the GC–ECNI-LRMS technique varied the most. The latter finding is disconcerting, as this technique is most commonly applied today, and should certainly be studied in more detail. GC–EI-MS/MS results varied as second most and caution is needed when using these latter two techniques.

No doubt, the number of laboratories that will analyse SCCPs, and most likely also MCCPs, will soon strongly increase. As MCCPs are reported in higher levels than SCCPs today [1], methods that differentiate SCCPs from MCCPs are essential to prevent spurious data. The classification of SCCPs as POPs by the Stockholm Convention and the ongoing very high production of these chemicals are reasons to finally overcome the analytical difficulties that have hindered analysts for a long time to properly analyse these compounds. The year 2017 has seen the first analytical congener standards without end-chlorination, with most likely more to follow. Whether it will be a congener-specific analysis or a more mathematical approach such as in the Bogdal et al. method [25], reliable methods are expected to become available in the next five years. And those are badly needed to determine the concentrations and effects of these compounds for the environment and human health. We strongly suggest to continue monitoring the between-laboratory comparability to assess consensus in SCCP analysis. For future exercises we suggest focussing not only on the choice of instrumental techniques but also on the quantification procedures, including the choice of standards, as well as the ability to separate SCCPs from other CPs and other compounds. We also recommend feedback to the participants to improve the quality of the analysis in the individual laboratories.

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Appendix A. Supplementary data

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